REMARKS

This Amendment is in response to the final Office Action mailed on April 1, 2009. Claim 1 is amended and is supported, for example, in the specification at page 11, line 35-page 12, line 3. No new matter is added. Claims 1-15 are pending with claims 16-28 being withdrawn.

Examiner Interview:

Applicants thank the Examiner Anna Verderame, for the telephonic interview that took place on July 9, 2009 with the Applicant's representative Amol Kavathekar. In the interview, Applicants asserted that neither the Ichihara reference nor the Berman reference teach that information is recorded by a change in the configuration of the titanium oxide. The Examiner noted that other cited prior art references, namely the Ozaki reference and the Furuya reference appear to teach a recording layer in which the titanium oxide changes state. The Examiner further noted that while these references only record on a single recording layer, it would be obvious to have multiple recording layers to record three-dimensionally. No consensus was reached.

§102 Rejections:

Claims 1 and 4-9 are rejected as being anticipated by Berman (US Patent No. 3,899,333). Claims 1 and 12 are rejected as being anticipated by Ichihara (US Patent No. 5,859,756). Claims 1-9 and 15 are rejected as being anticipated by Okazi (EP 0 924 094). Claims 1, 2, 4, 12 and 15 are rejected as being anticipated by Furuya (WO 00/13178 equivalent to US Patent No. 6,759,137). Claims 1-8 and 10 are rejected as being anticipated by Na (US Patent No. 6,576,589). These rejections are traversed.

Claim 1 is directed to an information recording medium that recites, among other features, a recording portion capable of storing information three-dimensionally only by irradiation with laser light. Claim 1 also recites that information is recorded by a change in configuration of the titanium oxide and the change in configuration of the titanium oxide is a change from an anatase type or a brookite type to a rutile type, or from an amorphous type to an anatase type, a brookite type, or a rutile type, or from a rutile type to an amorphous type, an anatase type, or a brookite type.

Berman does not disclose or suggest these features. In particular, nowhere does Berman disclose or suggest that information is recorded by a change in configuration of the titanium oxide and the change in configuration of the titanium oxide is a change from an anatase type or a brookite type to a rutile type, or from an amorphous type to an anatase type, a brookite type, or a rutile type, or from a rutile type to an amorphous type, an anatase type, or a brookite type. However, Berman merely discloses sensitizing dyes can be combined with the titanium oxide (see column 3, lines 33-34 of Berman). Nowhere does Berman even contemplate changing the state of its titanium oxide particles. For at least these reasons claim 1 is not disclosed by Berman and should be allowed. Claims 4-9 depend from claim 1 and should be allowed for at least the same reasons.

Ichihara also does not disclose or suggest the features of claim 1. Ichihara discloses in column 7, lines 52-60 that GeSbTe particles are dispersed in a TiO_2 matrix, and in column 12, lines 51-54 that the particles of the recording material are enclosed in a stable matrix. Thus, it appears that Ichihara discloses that the TiO_2 matrix is stable, and therefore does not change states. Nowhere does Ichihara contemplate that information is recorded by a change in configuration of the titanium oxide and the change in configuration of the titanium oxide is a change from an anatase type or a brookite type to a rutile type, or from an amorphous type to an anatase type, a brookite type, or a rutile type, or from a rutile type to an amorphous type, an anatase type, or a brookite type. For at least these reasons claim 1 is not disclosed by Ichihara and should be allowed. Claim 12 depends from claim 1 and should be allowed for at least the same reasons.

Okazi also does not disclose or suggest these features of claim 1. In the July 9, 2009 Examiner Interview, the Examiner asserts that the Ozaki reference appears to teach a recording layer in which the titanium oxide changes state. Okazi is directed to a process for preparing a resin-coated support for image recording with a polyolefin resin layer containing titanium dioxide provided thereon (see paragraph [0001] of Okazi). Nowhere does Okazi disclose or suggest that information is recorded by a change in configuration of the titanium oxide and the change in configuration of the titanium oxide is a change from an anatase type or a brookite type to a rutile type, or from an amorphous

type to an anatase type, a brookite type, or a rutile type, or from a rutile type to an amorphous type, an anatase type, or a brookite type.

Moreover, it appears that the titanium oxide in Okazi is used as a brightening agent contained in the resin-coated support for image recording. This is supported by prior art of the Okazi reference. In particular, column 5, line 48-column 6, line 3 of US Patent No. 3,501,298 discloses that TiO2 is combined with a brightener Uvitex OB (see the enclosed portion of US Patent No. 3,501,298, which is cited in US Patent No. 5,280,977, which corresponds to Japanese patent application JP 09(1997)-50093 cited in paragraph [0007] of Okazi, provided herewith). Also, the printing paper for photography is further coated with a photosensitive material (emulsion) or the like, and the photosensitive material reacts with light having a particular wavelength to form an image (column 1, line 60 of US Patent No. 3,501,298 and the Abstract of US Patent No. 5,280,977, which corresponds to Japanese patent application JP 09(1997)-50093 cited in paragraph [0007] of Okazi, provided herewith). For at least these reasons claim 1 is not disclosed by Okazi and should be allowed. Claims 2-9 and 15 depend from claim 1 and should be allowed for at least the same reasons.

Furuya also does not disclose or suggest the features of claim 1. Furuya is directed to an opto-magnetic recording medium that discloses a rutile type oxide (TiO_2) as an example of the material for a recording layer (see column 9, line 25-column 10, line 12 of Furuya). Nowhere does Furuya disclose or suggest that information is recorded by a change in configuration of the titanium oxide and the change in configuration of the titanium oxide is a change from an anatase type or a brookite type to a rutile type, or from an amorphous type to an anatase type, a brookite type, or a rutile type, or from a rutile type to an amorphous type, an anatase type, or a brookite type.

Further, it appears that Furuya cannot disclose or suggest that information is recorded by a change in configuration of the titanium oxide and the change in configuration of the titanium oxide is a change from an anatase type or a brookite type to a rutile type, or from an amorphous type to an anatase type, a brookite type, or a rutile type, or from a rutile type to an amorphous type, an anatase type, or a brookite type. In order for TiO_2 to undergo the change in configuration from a rutile type to an amorphous

type, an anatase type, or a brookite type, it is necessary that the TiO_2 reach 1800° C or higher (see, for example, page 11, line 35-page 12, line 13 of the present application).

In Furuya, the rutile-type oxide layer performs the function of cancelling undesirable compressive stress applied to a garnet ferrite layer by the tensile stress of the rutile-type oxide layer (see column 7, lines 44-49 of Furuya). However, in a magneto-optical recording medium, information is recorded by applying a strong external magnetic field to a material for a recording layer to invert the magnetization direction. When the magnetization direction is changed, the temperature of the recording material is raised to a Curie point or a particular temperature lower than the Curie point. However, the Curie temperature of TiO_2 doped with a small percentage of Co is 600 K (327° C) (see "Press Release 2008.11.5", provided herewith). Also, the Curie temperature of TiO_2 not doped with Co is likely 600 K (327° C) or slightly less than 600 K (327° C), as a ferromagnetic used as a magnetic material needs to still maintain a Curie temperature that is sufficiently higher than room temperature. Thus, as the Curie temperature of TiO_2 is much lower than 1800° C, Furuya cannot teach or suggest a change in configuration of the titanium oxide from a rutile type to an amorphous type, an anatase type, or a brookite type. For at least these reasons claim 1 is not disclosed by Furuya and should be allowed. Claims 4, 12 and 15 depend from claim 1 and should be allowed for at least the same reasons.

Na also does not disclose or suggest the features of claim 1. Na is directed to a method for making anatase type titanium dioxide photocatalyst. However, nowhere does Na disclose or suggest that information is recorded by a change in configuration of the titanium oxide. Accordingly, Na also cannot disclose or suggest that the change in configuration of the titanium oxide is a change from an anatase type or a brookite type to a rutile type, or from an amorphous type to an anatase type, a brookite type, or a rutile type, or from a rutile type to an amorphous type, an anatase type, or a brookite type. For at least these reasons claim 1 is not disclosed by Na and should be allowed. Claims 2-8 and 10 depend from claim 1 and should be allowed for at least the same reasons.

§103 Rejections:

Claims 13 and 14 are rejected as being unpatentable over Okazi in view of Alperovich (US Publication No. 2002/0098446). This rejection is traversed. Claims 13 and 14 depend from claim 1 and should be allowed for at least the same reasons described above. Applicants do not concede the correctness of this rejection.

Double Patenting:

Claims 1-9 and 11-15 are rejected under non-statutory obviousness-type double patenting as being unpatentable over claims 1-19 of Shiono (US Patent No. 7,313,080) in view of Ozaki. This rejection is traversed.

Claims 1-19 of Shiono teach an information recording medium comprising a recording portion capable of recording information three-dimensionally that requires a recording portion comprising at least one particle-containing layer. The particle-containing layer includes particles that absorb at least a part of light with a predetermined wavelength and are substantially transparent to recording light and reproducing light with wavelengths longer than the predetermined wavelength. The particles also have an absorption rate with respect to light with the predetermined wavelength being higher than the absorption rate with respect to the recording light and the reproducing light. The particle-containing layer also includes a particle-holding material that is substantially transparent to the recording light and the reproducing light. Claims 4 and 8 teach that the particle-holding material has an optical constant that changes at a predetermined temperature. Thus, when the temperature of the particle-containing layer increases to reach a predetermined temperature due to the heat generated by the light absorption of the particles, an optical constant of the particle-holding material changes to form information bits.

While claim 16 of Shiono teaches that the particles in the particle-containing board may include titanium oxide, nowhere do claims 1-19 of Shiono teach or suggest that information is recorded by a change in configuration of titanium oxide, as recited by claim 1. Also, nowhere doe claims 1-19 teach or suggest that the change in configuration of the titanium oxide is a change from an anatase type or a brookite type to a rutile type,

or from an amorphous type to an anatase type, a brookite type, or a rutile type, or from a rutile type to an amorphous type, an anatase type, or a brookite type.

Okazi does not overcome these deficiencies of Shiono. As discussed above, Okazi is directed to a process for preparing a resin-coated support for image recording with a polyolefin resin layer containing titanium dioxide provided thereon for use as a brightening agent. Nowhere does Okazi teach or suggest that information is recorded by a change in configuration of the titanium oxide or that the change in configuration of the titanium oxide is a change from an anatase type or a brookite type to a rutile type, or from an amorphous type to an anatase type, a brookite type, or a rutile type, or from a rutile type to an amorphous type, an anatase type, or a brookite type.

Conclusion:

Applicants respectfully assert that claims 1-28 are in condition for allowance. If a telephone conference would be helpful in resolving any issues concerning this communication, please contact Applicants' primary attorney-of record, Douglas P. Mueller (Reg. No. 30,300), at (612) 455-3804.

Respectfully submitted,

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Dated: August 3, 2009

By: _____
Douglas P. Mueller
Reg. No. 30,300
DPM/ahk

Panasonic Ref.: P031154-01
Your Ref.: 10873.1549USWO ; Our Ref.: H1780-04

Verification of Translation

PARTIAL TRANSLATION OF Press Release, published by New Energy and Industrial Technology Organization, Institute for Materials Research, Tohoku University

Title of the Invention:

Development of room temperature operating spintronics device material using room temperature ferromagnetic semiconductor
[Promotion of Industrial Technology Vol. 57]

I, Shin TANIMURA, professional patent translator, whose full post office address is IKEUCHI・SATO & Partner Patent Attorneys, 26th Floor, OAP Tower, 8-30, Tenmabashi, 1-Chome, Kita-ku, Osaka-shi, Osaka 530-6026, Japan am the translator of the document attached and I state that the following is a true partial translation to the best of my knowledge and belief of Press Release, published by New Energy and Industrial Technology Organization, Institute for Materials Research, Tohoku University.

At Osaka, Japan
DATED this July 30, 2009

Signature of the translator

Shin TANIMURA

Panasonic Ref.: P081154-01
Your Ref.: 10873.1549USWO ; Our Ref.: H1780-04

PARTIAL TRANSLATION OF Press Release, published by New Energy and Industrial Technology Organization, Institute for Materials Research, Tohoku University

Publication Date: November 5, 2008
Title: Development of room temperature operating spintronics device material using room temperature ferromagnetic semiconductor [Promotion of Industrial Technology Vol. 57]

[Newly announced matters]
(Lines 10–12)

An environmentally friendly material TiO_2, which does not influence human bodies and nature, is stable chemically, and displays ferromagnetism of about 600 K (Kelvin) merely by being doped with (addition of) several % of Co. Thus, TiO_2 can also be used for producing a thin film on a glass substrate by sputtering.

(Features)
(Lines 1–2)
・Co-doped TiO_2 is a ferromagnetic semiconductor having a Curie temperature of about 600 K.

[Outline of research results]
(Lines 13–16)
(1) Identify the basic physical properties of Co-doped TiO_2

It has been discovered that the Curie temperature of Co-doped TiO_2 is 600k (i.e., 327°C), which is far higher than room temperature. This extremely high Curie temperature among ferromagnetic semiconductors means that Co-doped TiO_2 is suitable for application at room temperature.

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United States Patent Office 3,501,298 Patented Mar. 17, 1970

3,501,298

PHOTOGRAPHIC PAPERS

Irvin H. Crawford, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

Filed Apr. 8, 1966, Ser. No. 541,204
Int. Cl. G03c 1/86, 1/76, 3/00
U.S. Cl. 96—85 4 Claims

ABSTRACT OF THE DISCLOSURE

Photographic elements have a support comprising a paper base having thereon polyolefin coating which contains titanium dioxide and bis(alkylbenzoxazole) thiophenes.

This invention relates to novel photographic elements. More particularly, this invention relates to black-and-white photographic papers of improved characteristics.

In its simplest form photographic paper is composed of paper sheet having black-and-white photographic emulsion thereon. This leaves much to be desired in brightness and smoothness, hence, for high quality photographic papers a baryta coating has been first applied over the paper sheet or base and a layer of photographic emulsion has been applied thereover. For obtaining dimensional stability and water-proofing, consideration has been given to the application of a clear polyethylene coating over the baryta layer upon which was coated a layer of photographic emulsion. This polyethylene layer while not interfering with the proper tint of the baryta coating resulted in a major loss in image sharpness in the prints obtained therefrom. Also previous baryta coated photographic papers have required ferrotyping by means of a heated polished surface to give glossiness as is ordinarily desired in photographic prints.

One object of my invention is to prepare black-and-white photographic papers having good dimensional stability, permanent surface characteristics and with a waterproofed base. Another object of my invention is to provide photographic papers which do not require ferrotyping in obtaining glossy prints therefrom. A further object of my invention is to prepare photographic papers having excellent tint and image sharpness. A still further object of my invention is to provide a base for photographic papers of good characteristics. Other objects of my invention will appear herein.

I have found that black-and-white photographic papers of good characteristics can be obtained, without the necessity of applying baryta coatings thereto, if the paper base is coated with a layer of polyethylene containing a substantial amount of titanium dioxide prior to applying a layer of the black-and-white photographic emulsion thereon. I have found that papers of even more improved characteristics are obtained by coating the paper with a polyethylene layer containing a substantial amount of titanium dioxide plus a blue, or a mixture of blue and magenta, pigment over the paper prior to applying the black-and-white photographic emulsion thereon. I have found that a further improved black-and-white photographic paper may be obtained if the paper base is coated with a polyethylene layer containing titanium dioxide, blue pigment and optical brightener prior to applying thereon a layer of black-and-white photographic emulsion.

The accompanying drawing illustrates photographic paper in accordance with my invention and with an additional layer of clear polyethylene on the backside of the paper base. This layer of clear polyethylene on the reverse side of the photographic element is desirable to further waterproof the paper base which is used.

The paper base employed in accordance with my invention may be any paper which has heretofore been considered useful for photographic paper particularly that having a high alpha-cellulose content. Particularly desirable is paper base to which wet strength has been imparted by the incorporation of wet strength resin. If the photographic emulsion to be applied is not adversely affected by formaldehyde the wet strength resin can be for example, melamine formaldehyde or urea formaldehyde resin. However, where photographic emulsion adversely affected by formaldehyde is used it is desirable to incorporate a non-aldehydic wet strength resin in the paper, for example cationic thermosetting polyamide - epichlorohydrin resin as described in U.S. Patent 2,926,154, available commercially under the name of "Kymene."

The polyolefin employed can be polyethylene or some other polyolefin such as polypropylene or propylene-ethylene copolymer. Although medium density polyolefin has been employed in this connection the use of polyolefins or polyethylenes of high density or low density is not excluded in products in accordance with the invention. The titanium dioxide used preferably is rutile TiO_2 ranging in particle size from 0.1–5 microns such as TiO_2 having average particle size of about 0.23 micron. The amount of titanium dioxide used should be substantial such as within the range of 3–15% by weight with preference given to the larger amounts of titanium dioxide (such as 10% or more) which can be accommodated in the coating operation used. One convenient means of applying the polyolefin coating to the paper is by means of extrusion coating wherein the melt of the polyolefin-TiO_2 composition is extruded onto the surface of the paper whereupon the coated surface is subjected to pressure by means of a chill roll. Instead of applying the polyolefin coating in this fashion it might be applied by means of a solution thereof in organic solvent followed by driving off the solvent such as by the use of a polished surface at elevated temperature or some other desired means. To assure good adhesion of the polyolefin coating to the paper, it is desirable that the paper be first treated to facilitate adhesiveness such as by electron bombardment or with a primer coat.

In addition to TiO_2 in the polyolefin coating, there may also be present in the compositions blue pigment, or a mixture of blue pigment and magenta pigment, which further improves the quality of the photographic prints obtained therewith. The amount of tint or colored pigment when used is kept minor ordinarily being no more than 1%, preferably a fraction of 1%. The pigments used should be non-wandering and compatible with the black-and-white photographic emulsion so as not to affect the sensitivity of the emulsion and do not wander from the polyolefin layer either to the emulsion layer or to the paper support. Also these pigments should be light stable and when extrusion coating is used they should exhibit heat stability.

Some pigments which are examples of pigments of this type and which are useful in TiO_2-polyolefin coatings in accordance with the invention are:

BLUE PIGMENTS

Ultra-Marine Blue EBEX

Manufacturer: Ultramarine Chemical Co.

Composition:	Percent
Silicon dioxide	37–50
Aluminum oxide	23–29
Sodium oxide	19–23
Sulfur	8–14

Description:
Vendor No. 59-3805.
Pigment Blue 29 Color Index 77007.

Shepard Cobalt Blue #3

Manufacturer: Shepard Co.
Composition: Stoichiometric Mixture of Cobalt Oxide and Aluminum Hydrate.
Description: Pigment Blue 28.

Cobalt Aluminated Blue V–3285

Manufacturer: Ferro Colors Corp.
Composition: Mixture of Cobalt Oxide and Aluminum Oxide.

MAGENTA PIGMENTS

Raspberry V–6260

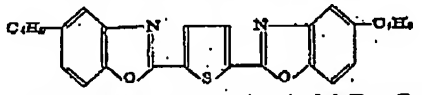
Manufacturer: Ferro Colors Corp.
Composition: Mixture of Cobalt Oxide and Phosphate Oxide.

Hostaperm Pink E–13–7000

Manufacturer: American-Hoechst Co.
Composition: Quinacridone Type Red.
Description: Pigment Red–122.

In addition to the pigments listed the polyolefin layer may also, if desired contain pigments such as barium sulfate, colloidal SiO_2, calcium carbonate and the like, although including these additional pigments may be dispensed with without adversely affecting the product obtained.

In addition, the polyolefin layer may contain an optical brightener, various of which are available at the present time used preferably in amounts within the range 0.02–0.50% by weight. Some brighteners which are available for use in polyolefins are described in U.S. Patent 2,784,184 and are marketed by the Geigy Industrial Company under the names Tinopal TCRP, Tinopal SFG, and Tinopal C. A brightener which has been found to be especially useful in polyolefin layers in accordance with the invention is a commercial material sold under the name "Uvitex OB" having the following chemical structure:



This material supplied by Ciba Chemical & Dye Company is described in Belgian Patent 612,775. Other brighteners which have been indicated as being useful in photographic products are described in U.S. Patent 2,639,990 of Kendall et al.

After the paper base has been coated with the layer comprising polyolefin and TiO_2 there is applied thereto a layer of a black-and-white photographic emulsion. To obtain good adhesion of the emulsion layer to the paper it is desirable that the paper coated with polyolefin be electron bombarded such as described in British Patent 971,058. In making the paper base to which the emulsion is applied the polyolefin layer is coated over the paper such as at the rate of 4–12 pounds per 1,000 square feet. To give a preferred product the same coverage of clear polyolefin coating may be applied to the reverse side of the paper sheet. In cases where the polyolefin coating is applied by the extrusion coating method, it has been found desirable to include therein a material which facilitates the coating operation. I have found that if the amide of a fatty acid, saturated or unsaturated, or the like be included in the composition in small amount aids the coating operation. If the coating is applied from solution in solvent particularly where the coated layer does not come in contact with some other surface, the coating improver may be dispensed with.

An advantage of the photographic papers and of the paper base useful as a base for photographic papers is that glossy prints may be obtained therewith without the use of ferrotyping. For instance, the use of a highly polished chill roll will give prints having good glossiness without the necessity of applying heat to the print.

The following examples illustrate my invention:

EXAMPLE 1

A wet strength paper which had been electron bombarded was coated by extrusion coating with a composition composed of 89.288 parts of medium density polyethylene (Tenite 2908), 0.162 part of Ultramarine Blue EBEX, 0.45 part of Raspberry Violet V–6260, 0.1 part of Armid O (oleylamide) and 10 parts of Du Pont Tipure R–100 titanium dioxide (rutile form) having an average particle size of 0.1 to 0.35 micron and was treated with a chilled highly polished metal roll. The thus obtained photographic paper base was electron bombarded and was coated with a gelatin-silver halide black-and-white photographic emulsion. The product was found, upon exposure and processing, to give photographic prints having good gloss and highly desirable characteristics.

EXAMPLE 2

A wet strength paper which had been electron bombarded was coated by extrusion coating with a composition composed of 89.265 parts of medium density polyethylene (Tenite 2908), 0.165 part of Ultramarine Blue EBEX, 0.47 part of Raspberry Violet V–6260, 0.1 part of Armid O (oleylamide) and 10 parts of Cabot RF–1 titanium dioxide (rutile form) whose average particle size was within the range of 0.1–0.35 micron and was treated with a chilled, highly polished metal roll. The thus obtained photographic paper base was electron bombarded and was coated with gelatin-silver halide black-and-white photographic emulsion. The product obtained, upon exposure and processing, was found to give photographic prints having good gloss and highly desirable characteristics.

EXAMPLE 3

A wet strength paper which had been electron bombarded was coated by extrusion coating with a composition composed of 89.7349 parts of medium density polyethylene (Tenite 2908), 0.1640 part of Ultramarine Blue EBEX, 0.0011 part of Hostaperm Pink E, 0.10 part of Armid O (oleylamide) and 10 parts of Du Pont R–100 titanium dioxide and was treated with a chilled highly polished metal roll. The thus obtained photographic paper base was electron bombarded and was coated with gelatin-silver halide black-and-white photographic emulsion. The product obtained, upon exposure and processing, was found to give photographic prints having good gloss and highly desirable characteristics.

EXAMPLE 4

A wet strength paper which had been electron bombarded was coated by extrusion coating with a composition composed of 89.1789 parts medium density polyethylene (Tenite 2908), 0.1652 part of Shepard Cobalt Blue #3, 10 parts of Du Pont R–100 titanium dioxide, and 0.7559 part Raspberry Violet V–6260 and was treated with a chilled highly polished metal roll. The thus obtained photographic paper base was electron bombarded and then was coated with gelatin-silver halide black-and-white photographic emulsion. The product obtained, upon exposure and processing, was found to give photographic prints having good gloss and highly desirable characteristics.

EXAMPLE 5

A wet strength paper which had been electron bombarded was coated by extrusion coating with a composition composed of 89.82985 parts of medium density polyethylene (Tenite 2908), 10 parts of Du Pont R–100 titanium dioxide, .16520 part of Shepard Cobalt Blue #3, and .00495 part of Hostaperm Pink E and was treated with a chilled highly polished metal roll. The thus obtained photographic paper base was electron bombarded and then was coated with gelatin-silver halide

black-and-white photographic emulsion. The product obtained, upon exposure and processing, was found to give photographic prints having good gloss and highly desirable characteristics.

In each of the above Examples 1–5, the paper was coated on the reverse side with a coating of clear polyethylene.

EXAMPLE 6

A wet strength paper which had been electron bombarded was extrusion coated with the following composition:

	Percent
Medium density polyethylene	89.75
TiO_2, Du Pont R–100	10.00
Ultramarine Blue EBEX	0.10
Armid O	0.10
Uvitex OB	0.125

The coating was applied to the paper at the rate of 7.6 lb./1000 ft.^{2} and was treated with a chilled highly polished metal roll. A clear polyethylene coating was extrusion coated at the rate of 4.5 lb./1000 ft.^{2} to the wire side of the paper. The pigmented coat was electron bombarded and a layer of a black-and-white gelatino silver halide photographic emulsion was applied thereover. The product was exposed and processed. Photographic prints of good quality were obtained.

EXAMPLE 7

A wet strength paper which had been electron bombard was extrusion coated with the following composition:

	Percent
Medium density polyethylene	89.6375
Titanium dioxide, R–100	10.0000
Ultramarine Blue EBEX	0.1125
Raspberry V–6260	0.0300
Uvitex OB	0.2200

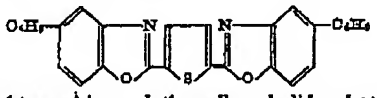
The coating was applied to the paper at the rate of 7.6 lb./1000 ft.^{2} and was treated with a chilled highly polished metal roll. A clear polyethylene coating was extrusion coated at the rate of 4.5 lb./1000 ft.^{2} to the wire side of the paper. The pigmented coat was electron bombarded and a layer of a black-and-white gelatino silver halide photographic emulsion was applied thereover. The product was exposed and processed. Photographic prints of good quality were obtained.

Uvitex OB is an outstanding brightener in products in accordance with the invention in combination with TiO_2 because it does not depend on ultra-violet light for its peak excitation, hence, its effectiveness is not diminished by the presence of TiO_2.

The invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended claims.

I claim:

1. A photographic element comprising a support which includes a paper base having on and firmly adhered to one surface thereof a layer of polyolefin which contains about 3–15% by weight titanium dioxide and about 0.02–0.50% by weight optical brightener having a structure represented by the formula:



and a light sensitive gelatino silver halide photographic emulsion firmly adhered to said polyolefin layer.

2. The invention according to claim 1 and wherein said polyolefin is polyethylene and on and firmly adhered to the other surface of the paper base is a plastic coating.

3. The invention according to claim 1 and wherein said polyolefin is polyethylene which contains blue pigment in addition to the optical brightener and titanium dioxide, and on and firmly adhered to the other surface of the paper base is a polyethylene coating.

4. The invention according to claim 1 and wherein said polyolefin is polyethylene which contains blue pigment and magenta pigment in addition to the titanium dioxide and optical brightener, and on and firmly adhered to the other surface of the paper base is a polyethylene coating.

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3,406,070 10/1968 Ostiker et al. ..... 96—82

NORMAN G. TORCHIN, Primary Examiner

J. R. HIGHTOWER, Assistant Examiner.

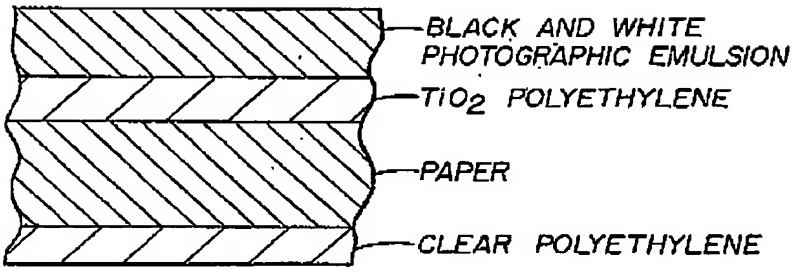
U.S. Cl. X.R.

96—67; 117—155

March 17, 1970 I. H. CRAWFORD 3,501,298

PHOTOGRAPHIC PAPERS

Filed April 8, 1966



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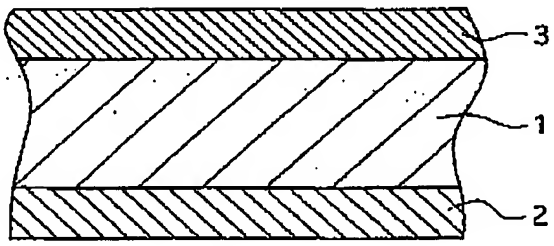
(54)【発明の名称】 写真印画紙用支持体

(57)【要約】

【課題】 耐水性樹脂層の膜割れ、ダイリップ筋等の発生がなく、基体との密着性に優れ、しかも画像の鮮鋭性に優れる写真印画紙用支持体の提供。

【解決手段】 基体１の両面に耐水性樹脂層２，３を有する写真印画紙用支持体において、乳剤を塗布する側の耐水性樹脂層２又は３が二酸化チタン顔料を含有している。この二酸化チタン顔料は、二酸化チタン粒子表面をシランカップリング剤により処理したものが使用される。望ましくは、二酸化チタン粒子の表面を無機表面処理剤で処理し、その後、シランカンプリング剤で処理したものがよく、シランカンプリング剤としては、シリコーンオリゴマーが望ましい。



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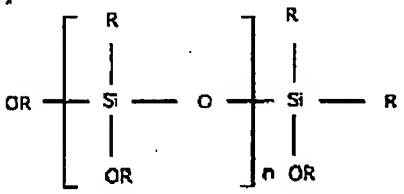
【特許請求の範囲】

【請求項1】 基体の両面に耐水性樹脂被覆層を設けてなる写真印画紙用支持体において、少なくとも乳剤を塗布する側の耐水性樹脂被覆層中に、二酸化チタン顔料を含有し、該二酸化チタン顔料の粒子表面がシランカップリング剤で被覆処理された二酸化チタン顔料であることを特徴とする写真印画紙用支持体。

【請求項2】 前記シランカップリング剤が、下記の一般式で示されるシリコーンオリゴマーである請求項1に記載の写真印画紙用支持体。

【化1】



（上記一般式中、n＝1～5、R＝CH_3 又はC_2H_5）

【請求項3】 前記二酸化チタン顔料が、シランカップリング剤による処理の前に二酸化チタンを無機表面処理剤で処理されたものである請求項1に記載の写真印画紙用支持体。

【請求項4】 前記二酸化チタンに対するシリコーンオリゴマーの表面処理量が0．01～5重量部である請求項2に記載の写真印画紙用支持体。

【請求項5】 前記無機表面処理剤が、Al_2O_3 又はSiO_2の少なくとも1つからなる請求項3に記載の写真印画紙用支持体。

【請求項6】 二酸化チタンに対し、無機表面処理剤の処理量が無水物の形で計算して0．01～1．8重量%で処理されたものである請求項3又は請求項5に記載の写真印画紙用支持体。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は写真印画紙支持体に関し、特に基体の両面に耐水性樹脂被覆層を設けてなる写真印画紙用支持体に関し、画像の鮮鋭性（解像力）、表面特性に優れた写真用支持体に関する。

【0002】

【従来の技術】従来、写真印画紙用支持体として、その両面を樹脂で被覆したものが知られており、特に、乳剤塗布側の被覆層には、二酸化チタン、顔料、ブルーイング剤（青色顔料も含む）、蛍光増白剤などが含有される（米国特許第3501298号公報）。

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【0003】この場合に使用する二酸化チタンは、耐水性と共に光反射効率を高める作用を有するが、この二酸化チタンの含有量を増加させれば増加させる程、画像解像力が向上することが知られている。

【0004】ところで、この耐水性樹脂層を形成するに際しては、二酸化チタンを含有する耐水性樹脂をスリットダイから短時間でフィルム状に溶融押し出ししているが、樹脂被覆中に20重量%以上の二酸化チタンを含有させ、従来の如く290～350℃の吐出温度で溶融押し出しを行った場合には、耐水性樹脂層の割れ（以下、膜割れという）を生じたり、押出機ダイリップ部に筋（以下、ダイリップ筋という）が発生し易くなる。

【0005】そして、このような膜割れが発生すると、製品の外観を著しく損なうのみならず、耐水性も失うため商品価値が無くなり、また、ダイリップ筋が発生すると、製造されたフィルム或いは積層物の表面に縦方向に連続的なスジが生ずるので、製品の外観を著しく損なうばかりでなく、延伸などの二次加工時においてもフィルムの透明度にムラが発生し、商品価値を著しく低下させる。

【0006】そこで、こうした欠点を改善するために、吐出温度を290℃未満にした場合には紙基体と耐水性樹脂間の密着力が著しく低下し、また、溶融した耐水性樹脂の流動性も下がるため、押し出しラミネート時のクーリングロールの同伴エアーがクーリングロールとプレスロール間のニップ部2に浸入した時、その同伴エアーが行き場を失い溶融した耐水性樹脂を押すことによって、発生する凹状故障、これが発生すると平面性が悪くなる。さらに耐水性樹脂層にクレータが発生しやすい。従って、従来は、解像力を犠牲にしても、二酸化チタンの含有量を20重量%以下に抑制するという方法が採られていた。

【0007】ところが、最近、二酸化チタン含有層に粘着付与剤樹脂を添加し、175～290℃の吐出温度で溶融押し出しすることにより、二酸化チタンの含有量を増加させた高解像力印画紙用支持体が開発された（国際公開番号：WO92／17538）。

【0008】

【発明が解決しようとする課題】そこで、本発明者等は、上記の高解像力印画紙用支持体について詳細に検討したところ、この方法では、二酸化チタンの分散性が充分でないのみならず、押し出しラミネート後の冷却ロールからの剥離性が悪いために、製品の外観不良が発生し易いことが判明した。

【0009】

【課題を解決するための手段】本発明者等は、より確実に、高解像力印画紙用支持体を製造するために鋭意検討した結果、膜割れ及びダイリップ筋の発生は、樹脂組成物中の二酸化チタンに吸着あるいは結合している水分に左右されることがわかり、使用する二酸化チタンの粒子

US005820977A

United States Patent [19]

Shirakura et al.

[11] Patent Number: 5,820,977

[45] Date of Patent: Oct. 13, 1998

[54] SUPPORT FOR PHOTOGRAPHIC PRINTING PAPER COMPRISING SILICONE COATED TITANIUM DIOXIDE PIGMENTS

[75] Inventors: Yuji Shirakura; Hisamasa Abe, both of Shizuoka, Japan

[73] Assignee: Fuji Photo Film Co., Ltd., Kanagawa, Japan

[21] Appl. No.: 681,511

[22] Filed: Jul. 23, 1996

[30] Foreign Application Priority Data

Aug. 4, 1995 [JP] Japan 7-200099

[51] Int. Cl.[6] B32B 5/16

[52] U.S. Cl. 428/328; 428/405; 428/407

[58] Field of Search 428/328, 403, 428/407, 405

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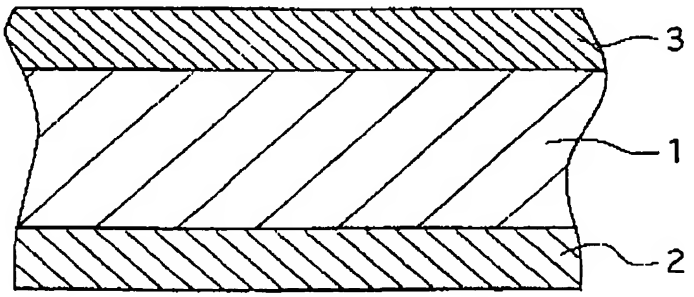
Primary Examiner—H. Thi Le

Attorney, Agent, or Firm—Sughrue, Mion, Zinn, Macpeak & Seas, PLLC

[57] ABSTRACT

In a support for a photographic printing paper, in which water-proof resin layers 2, 3 are formed on both sides of a base 1, one of the water-proof resin layers 2, 3, at a side of an emulsion to be coated, contains titanium dioxide pigment. The surface of particles of the titanium dioxide pigment is treated with a silane coupling agent. Preferably, the surface of titanium dioxide is subjected to surface treatment with an inorganic surface treating agent, and subsequently, is treated with the silane coupling agent. Further, silicone oligomer is preferably used as the silane coupling agent. As a result, a support for a photographic printing paper can be provided which causes no film fractures in the water-proof resin layers and no score lines in a die-lip portion, provides excellent adhesiveness to the base, and is superior in image sharpness.

16 Claims, 3 Drawing Sheets



SUPPORT FOR PHOTOGRAPHIC PRINTING PAPER COMPRISING SILICONE COATED TITANIUM DIOXIDE PIGMENTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a support for a photographic printing paper, and particularly to a support for a photographic printing paper in which water-proof resin coating layers are formed on both sides of a base and which is superior in image sharpness (i.e., resolving power) and in a surface characteristic.

2. Description of the Related Art.

Conventionally, there has been known a support for a photographic printing paper, of which both sides are coated with resin. Particularly, a coating layer of the support provided on the side of an emulsion to be coated comprises titanium dioxide, pigments, a bluing agent (including blue pigments), a fluorescent brightening agent, and the like (see U.S. Pat. No. 3,501,298).

The titanium dioxide used in this case has a function of improving light reflection efficiency as well as the water-proof property. It has been known that the resolving power improves as an amount of titanium dioxide contained is increased.

On the other hand, the water-proof resin layer is formed in such a manner that a water-proof resin containing titanium dioxide is melt-extruded from a slit die in the shape of a film in a short time. However, when the resin coating layer contains at least 20% by weight of titanium dioxide and is melt-extruded at an extrusion temperature in the range from 290° C. to 350° C. in a conventional manner, fractures are formed in the water-proof resin layer (the fractures will be hereinafter referred to as film fractures), or a score line is apt to be formed in a die lip portion of an extruder (the score line will be hereinafter referred to as die-lip score line).

When such film fractures are formed, not only the appearance of a product is markedly deteriorated, but also the water-proof property is lost, thereby resulting in loss of commercial value of the product. Further, when die lip score lines are caused, continuous streaks are formed on a surface of a manufactured film or a laminated layer in the longitudinal direction. For this reason, not only the appearance of the product is markedly deteriorated, but also unevenness in the transparency of the film occurs even at the time of a secondary process of resin, such as a drawing process. As a result, the commercial value of the product is markedly lowered.

When the extrusion temperature is set at a temperature of less than 290° C. in order to solve the above-described drawbacks, adhesion force between a paper base and the water-proof resin is markedly reduced and the flowability of the molten water-proof resin also deteriorates. Here, when air carried on a cooling roll at the time of extruding and laminating processing enters a nip portion between the cooling roll and a press roll, the air cannot be released and pushes the molten water-proof resin, thereby causing a defect in the shape of a dent on the surface of the water-proof resin. The occurrence of this defect would lead to deterioration in planeness. In addition, a crater is apt to be formed in the water-proof resin layer. Accordingly, a method has been conventionally used in which, at the sacrifice of the resolving power, the content of titanium dioxide is limited to be less than 20% by weight.

On the other hand, recently, there has been developed a support for a photographic printing paper having high resolving power, in which a tackifier resin is applied to a layer containing titanium dioxide and the resultant layer is melt-extruded at an extrusion temperature in the range from 175° C. to 290° C., with the result that the content of titanium dioxide is increased (see PCT International Publication No. WO92/17538).

Further, in Japanese Patent Publication (JP-B) No. 61-26652, there is described a method for manufacturing a photographic coating paper in which polyolefin resin containing titanium dioxide subjected to surface treatment with organopolysiloxane is melt-extruded and a paper is coated with the resin. It is an object of the invention of this publication to prevent deterioration of the quality of a surface of the coating paper due to contamination of a die-lip portion.

In the specification of the above-described Japanese Patent Publication, examples of the organopolysiloxane are dimethylpolysiloxane, dimethylhydrodienesiloxane, and the like. However, these materials do not have coupling groups as end groups thereof and are not silane coupling agents. These materials are compared with the present invention as shown in Comparative Examples 3 and 4 which will be shown later and do not have such an effect as obtained in the silane coupling agent used in the present invention.

The present inventors had studied in detail the above-described support for a photographic printing paper having high resolving power. As a result, it has been revealed that, in this method, not only the dispersibility of titanium dioxide is not sufficient, but also peeling property of the resin layer from the cooling roll after extruding and laminating processing is deteriorated, so that the appearance of the product tends to become inferior.

SUMMARY OF THE INVENTION

The present inventors had diligently studied for reliably manufacturing a support for a photographic printing paper having high resolving power, and as a result, they have found that occurrence of film fractures and die-lip score lines can be influenced by water adsorbed on or bonded to titanium dioxide in a resin composition and that, by using a titanium dioxide pigment in which the surface of titanium dioxide particles to be used is subjected to coating with a silane coupling agent, titanium dioxide pigment in an amount of at least 20% by weight can be easily contained in a polyolefin resin layer. In addition, it has also been found that, even when extrusion molding is performed at a melting temperature of 325° C. or thereabouts, film fractures, die-lip score lines and the like are not caused and adhesiveness is sufficiently maintained, with the result that the present invention has been achieved.

Namely, the present invention is a support for a photographic printing paper, with water-proof resin coating layers being formed on both sides of a base, wherein a titanium dioxide pigment is contained in at least one of the water-proof resin coating layers at a side of an emulsion to be coated and the surface of particles of the titanium dioxide pigment is subjected to coating treatment with a silane coupling agent, and silicone oligomer which will be described later is desirably used as the silane coupling agent.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a principal portion of a support for a photographic printing paper according to Example 1 of the present invention.

FIG. 2 is a cross-sectional view of a principal portion of a support for a photographic printing paper according to Example 2 of the present invention.